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PATENT ABSTRACTS OF JAPAN

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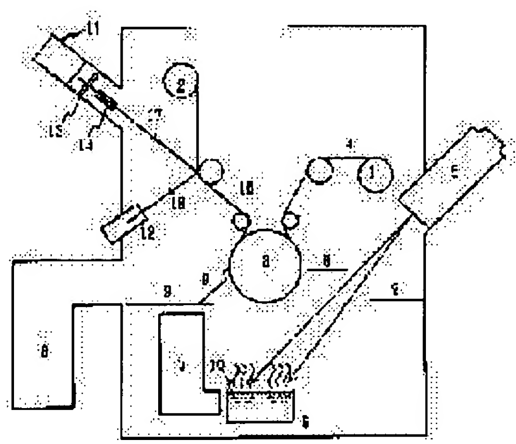
(54) METHOD FOR PRODUCING GAS BARRIER FILM AND DEVICE THEREFOR

(57)Abstract:
PURPOSE: To monitor the thickness of even a gas barrier film using a colorless and transparent thin film, a multiple-oxide thin film, etc., and hence to impart a uniform characteristic in the longitudinal direction by measuring the characteristic X ray intensity of the element constituting a thin film released after an atom forming an inorg. thin film is excited.



CONSTITUTION: The vapor-deposition source material 10 in a crucible 6 is irradiated with an electron beam from an electron gun 5, the material 10 is deposited on a plastic substrate 4 delivered from a rewinding roll 1 to form an inorg. thin film 16 on the substrate 4, and a gas barrier film 15 is obtained. The inorg. film 16 of the gas barrier film 15 is irradiated with an exciting X ray 17 generated from its source 11 while limiting the diameter of the X ray with a collimator 14, and the intensity of the characteristic X ray 18 emitted at that time is measured by a detector 12. The data thus obtained are inputted to a personal computer, the difference from the command is fed back to the emission current, etc., of the electron gun 5, and the gas barrier film 15 is

obtained.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] It is related with the manufacture method of a gas barrier film of having the property which was excellent as the wrapping of which the airtightness of food, drugs, electronic parts, etc. is required, or a gas cutoff material of industrial use, and a manufacturing installation.
[0002]
[Description of the Prior Art] the gas barrier film which consists of inorganic thin films which have the gas barrier property prepared on the plastics base material and this base material -- a vacuum deposition method, a sputtering technique, and CVD (chemical vapor deposition) -- it is made by the producing methods, such as law, and, generally roll coater type equipment is used. As a method of acting as the monitor of the thickness of the gas barrier thin film (inorganic thin film) produced at this time, a visible ray is irradiated at the thin film concerned, that permeability, a reflection factor, or an absorption coefficient is searched for, and the method of presuming thickness from that value is used. Conventionally, although the most common oxidation silicon (SiOX:x =1.3-1.8) thin film system gas barrier film as a gas barrier film using an inorganic thin film is transparent, it is presenting brown, and it is effective also by the thickness monitor method using a visible ray. Moreover, the thickness data of the thin film for which it asked by the thickness monitor method by this visible ray is fed back, and the method and manufacturing installation which are used for management of the production process of a gas barrier film are known.
[0003]
[Problem(s) to be Solved by the Invention] Above-mentioned SiOX which wears brown a little There is a problem that change of visible-ray permeability is very small, its thickness change of about 100A is inadequate as a precision of thickness measurement, and the precision of feedback by the production process does not go up by the case of a thin film system gas barrier film, either. Moreover, change of the visible-ray permeability according to the thickness of a thin film with multiple oxide thin film system gas barrier films, such as a gas barrier film using transparent and colorless thin films, such as an aluminum oxide and a magnesium oxide, the aluminum oxide and oxidation silicon system which are proposed recently, and a magnesium oxide, an oxidation silicon system, is small, and control of the thickness of a thin film is in an almost impossible condition by the thickness monitor method using the conventional visible ray. Furthermore, when the multiple oxide is being used as the gas barrier thin film, by the conventional monitor method, the information about the homogeneity of a presentation is not acquired at all.
[0004] Thus, since there is no effective thickness monitor method in the production process of the gas barrier film using a transparent and colorless thin film, a multiple oxide thin film, etc., there is a problem that control of the evaporation rate in online is impossible, and the property (various kinds of properties including oxygen barrier property and a voile property) of the produced gas barrier film cannot be guaranteed.
[0005] The purpose of this invention is offering the manufacturing installation and the manufacture

method of a gas barrier film of having the effective thickness monitor method also to the gas barrier film using a transparent and colorless thin film, a multiple oxide thin film, etc.
[0006]
[Means for Solving the Problem] this invention persons found out that the above-mentioned purpose was attained by this invention. That is, acting as the monitor of the thickness of the thin film concerned by measuring characteristic-X-ray reinforcement of at least one element among characteristic X ray of an element of the thin film presentation concerned released after making into an excitation state an atom which forms an inorganic thin film, this invention is the manufacture method of a gas barrier film characterized by preparing an inorganic thin film on a plastics base material it runs to continuation, and is the manufacturing installation of the gas barrier film concerned.
[0007] A plastics base material in this invention carries out melting extrusion of the organic macromolecule, and means a thing of plastic film which gave extension, cooling, and heat setting a longitudinal direction and/or crosswise if needed. It is desirable still more desirable that the thickness is 5-500 micrometers, and the plastic film concerned is 8-200 micrometers.
[0008] As the above-mentioned organic macromolecule, polyethylene, polypropylene, polyethylene terephthalate, polyethylene -2, 6-naphthalate, nylon 6, nylon 4, Nylon 66, Nylon 12, a polyvinyl chloride, a polyvinylidene chloride, polyvinyl alcohol, all aromatic polyamide, polyamidoimide, polyimide, polyether imide, polysulfone, a polyphenylene sulfide, polyphenylene oxide, etc. are mentioned. Moreover, what carried out little copolymerization of other organic macromolecules, or was blended is sufficient as these organic macromolecules. A well-known additive, for example, an ultraviolet ray absorbent, an antistatic agent, a plasticizer, lubricant, a coloring agent, etc. may be added by the organic macromolecule concerned.
[0009] Moreover, plastic film by which could perform surface treatment, such as processing by silane coupling agent or primers (a polyester system, a polyurethane system, acrylic, silicon system, etc.), corona discharge treatment, and low-temperature plasma treatment, to at least one side of the above-mentioned base material for the purpose which raises adhesion force of a vacuum evaporationo film etc., or uniaxial stretching was carried out as a base material may be used. Furthermore, a base material may be heated during vacuum evaporationo or after vacuum evaporationo for stabilization of a vacuum evaporationo film presentation, or improvement in adhesion force.
[0010] If an inorganic thin film used by this invention has gas barrier property, there will be especially no limit. As the material, nitride; sulfide; carbide, such as oxide; alumimium nitride, such as semiconductor; aluminum oxides, such as metal; silicon, such as aluminum, nickel, chromium, iron, cobalt, zinc, gold, silver, and copper, germanium, and carbon, oxidation silicon, a magnesium oxide, a calcium oxide, zirconium oxide, titanium oxide, boron oxide, an oxidation hafnium, and a barium oxide, boron nitride, and magnesium nitride, etc. is mentioned. Oxides, such as an aluminum oxide, oxidation silicon, a magnesium oxide, a calcium oxide, zirconium oxide, and titanium oxide, things which added or replaced a metal, a semiconductor, etc. by them or those mixture, etc. are desirable as a transparence gas barrier thin film.
[0011] Although there will be especially no limit if thickness of an inorganic thin film is thickness useful as gas barrier, 30-10000A is 70-8000A still more preferably preferably. Moreover, it is not necessary especially to be colorlessness also about a color.
[0012] Although a gas barrier film in this invention mainly consists of a plastics base material and an inorganic thin film, it formed well-known adhesives conventionally on an inorganic thin film further, and could carry out the laminating of the plastic film on it.
[0013] They are the adhesives which adhesives which consist of a natural rubber system, a synthetic-rubber system, a polyester system, a polyurethane system, acrylic, silicone systems, etc. such mixture, etc., for example are mentioned as adhesives used, and consist of polyurethane, polyester, poly isocyanates, or such mixture preferably. 0.5-20 micrometers of thickness of the adhesives concerned are 0.5-10 micrometers still more preferably preferably.
[0014] Moreover, what was mentioned above as plastic film by which a laminating is carried out is mentioned, and 5-500 micrometers of thickness of the film concerned are 8-300 micrometers still more

preferably preferably.
[0015] Although there is especially no limit as the manufacture method of a gas barrier film in this invention except for a method of acting as the monitor of the thickness of a thin film, it is a method of forming dry processes, such as a vacuum deposition method, a sputtering technique, and a CVD method, desirably.
[0016] For example, vacuum deposition is a method of heating a material included in a crucible, evaporating it with beam heating of resistance heating, high frequency induction heating, an electron ray, an ion beam, etc., making it adhering to base materials (plastic film etc.), and obtaining a thin film. In that case, heating temperature and a heating method change with a material, purposes, etc., and reactant vacuum deposition which makes oxidation reaction etc. cause can also be used.
[0017] Moreover, a sputtering technique is a method of introducing discharge gas (argon etc.) in a vacuum tub, applying high-frequency voltage or direct current voltage between a target and base materials (plastic film etc.), plasma-izing discharge gas, flying a target material by making it colliding with a target, making it adhering to a substrate, and obtaining a thin film. Moreover, a reactant sputtering technique which reactant gas, such as oxygen, is introduced [sputtering technique] and makes oxidation reaction cause may be used. The same is said of a CVD method.
[0018] An example is given and a thickness monitor method of an inorganic thin film in this invention is explained below.
** Restrict area by collimator and irradiate an X-ray which generated W, Mo, Rh, Cr, etc. from an X-ray tube used as a target first as a source of excitation at an inorganic thin film.
[0019] Although a diameter of a spot of an X-ray irradiated at this time is prescribed by area to measure and precision of feedback demanded and is not limited especially, its 1-50mm is desirable. Moreover, especially a method of making an excitation state an atom which forms an inorganic thin film is not restricted, but electron beam irradiation, radiation irradiation, laser radiation, etc. are mentioned in addition to X-ray irradiation.
[0020] ** An atom which forms a thin film can irradiate an X-ray etc., will be in an excitation state, and when returning to a ground state after that, it emits fluorescence X rays (characteristic X ray) of a proper to each element. The spectrum of this emitted characteristic X ray is carried out, and it detects by detecting element.
[0021] Distributed process input output equipment which used diffraction phenomena by analysing crystals and diffraction gratings, such as graphite, lithium fluoride, and a sodium chloride, as this spectrum and a detecting element, non-distributed process input output equipment by pulse-height-analysis method which uses a detector with an output proportional to energy of a measurement X-ray, or whichever is sufficient. Moreover, as a characteristic-X-ray detector, a gas multiplication proportional counter, a semiconductor detector, a scintillation detector, etc. can be used.
[0022] Characteristic X ray is an X-ray constituted by a line spectrum peculiar to each element, or its part here, and it is also called characteristic X-rays. As wavelength of this characteristic X ray, 1.542A and K alpha rays of Mo are 0.710A, and wavelength of K alpha rays of aluminum, Si, Mg, and calcium of K alpha rays (X-ray emitted when an electron changes from an L shell to empty level of a K edge shell by kind of characteristic X ray) of Cu is 8.339A, 7.126A, 9.889A, and 3.360A, respectively, for example.
[0023] Characteristic-X-ray reinforcement of an element which forms an inorganic thin film obtained as mentioned above has thickness and a correlation of a thin film, and thickness measurement of it becomes possible from a calibration curve which measured and produced characteristic-X-ray reinforcement with a sample of thickness known beforehand. Namely, what is necessary is just to measure characteristic-X-ray reinforcement of at least one element in an element contained in a thin film. Moreover, information about a thin film presentation is also acquired by taking an intensity ratio of characteristic X ray of two or more configuration elements.
[0024] ** Feed back the result to vacuum evaporationo conditions as mentioned above at the same production process as vacuum evaporationo of a up to [a plastics base material], performing a thickness monitor of a thin film.

[0025] As vacuum evaporationo conditions, an emission current of an electron gun (henceforth EB gun), a scanning speed, film advance speed, etc. are mentioned. That is, while thickness is increasing, for example, EB power is lowered as vacuum evaporationo conditions. Conversely, while thickness is decreasing, by raising EB power, dispersion in thickness can be suppressed and thickness can be kept constant. Moreover, since data about a thin film presentation is also obtained from an intensity ratio of characteristic X ray of two or more elements, by the producing method for the ability to perform feedback to each presentation like plural system vacuum evaporationo, a presentation ratio can also be maintained at stability by feeding back.

[0026] Here, drawing 1 is drawing showing one example of a gas barrier film manufacturing installation of this invention, and explains a manufacture method of a gas barrier film of this invention using this drawing. The plastics base material 4 which irradiated an electron beam, began to wind around the source material 10 of vacuum evaporationo included in a crucible 6 from the EB gun 5, and was sent out from a roll 1 is made to vapor-deposit the source material 10 of vacuum evaporationo. Thereby, the inorganic thin film 16 is made to form on the plastics base material 4, and the gas barrier film 15 is obtained. Next, X-ray 17 for excitation generated from the X line source 11 for excitation is irradiated on the inorganic thin film 16 of the gas barrier film 15, restricting the diameter by collimator 14, and reinforcement of the characteristic X ray 18 then emitted is measured with the characteristic-X-ray detector 12. This obtained data is put into a personal computer, and the gas barrier film 15 is produced, feeding back a difference with desired value to an emission current of the EB gun 5 etc.

[0027]

[Example] This invention is not limited by these, although an example is raised to below and this invention is explained to it.

[0028] Moreover, the measuring method of the thickness in the sample from which the gas barrier film produced in the following example and the example of a comparison was taken out, and oxygen transmittance, and the method of a component analysis are as follows.

** Thickness (thickness of an inorganic thin film)

It measured using X-ray fluorescence equipment (the Rigaku make, system 3270). Generating of an X-ray was performed by 50kV and 50mA using the rhodium bulb.

** Oxygen transmittance (oxygen transmittance of a gas barrier film)

It measured at the room temperature using oxygen transmissometry equipment (the product made from modern conte RORUZU, OX-TRAN100).

** Component analysis (ICP atomic absorption analysis)

a sample -- combustion and ashing -- it melted to sodium carbonate the back and the quantum was carried out after solution-izing using RF inductively-coupled-plasma-atomic-emission-spectrometry equipment (the Shimadzu make and ICPS-2000 mold).

[0029] The aluminum oxide thin film was formed with electron beam vacuum deposition on the polyethylene terephthalate (PET) film (the product made from Toyobo Co., Ltd. , E5100) of 12-micrometer thickness, using the aluminum oxide (aluminum 2O3, 99.5% of purity) of the shape of a particle with a magnitude of about 3-5mm as a source of example 1 vacuum evaporationo. The emission current of about 100 m/min and EB gun was made into near 1.2A, and aim thickness made film advance speed 500A. The white X-rays generated from the X-ray tube as a thickness monitor were restricted to the diameter of 30mm by the collimator, and the aluminum-oxide thin film was irradiated. At this time, the aluminum atom which forms a thin film would be in the excitation state, and when returning to a ground state after that, it emitted characteristic X ray with a wavelength of 8.339A. This reinforcement is measured with a scintillation counter and it enabled it to convert into a thickness value automatically by the calibration curve which was being prepared beforehand. The gas barrier film was produced having put the output from this thickness monitor into the personal computer, and feeding back a difference with desired value to the emission current of EB gun etc. Thus, the sample of the place of 2000, 4000, and 6000m was started from the vacuum evaporationo starting position of the produced gas barrier film, and thickness and oxygen transmittance were measured. The result is shown in a table 1. Thickness was fixed, oxygen barrier property was good, and the long transparence gas barrier film with

a uniform oxygen barrier property was obtained in the length direction so that it may understand from now on.
[0030]
[A table 1]

実施例１

フィルム位置 (m)	膜　厚 (Å)	酸素透過度 (cc/m^2.24hr.atm)
２０００	５００	３．５
４０００	５１０	３．７
６０００	４９０	３．５
８０００	５１０	３．８
１００００	５００	３．６

[0031] Although the aluminum oxide thin film system gas barrier film was produced with electron beam vacuum deposition like example of comparison 1 example 1, especially the monitor of thickness did not carry out but aim thickness could be 500A. It sampled every 2000m from the vacuum evaporationo starting position like the example 1, and thickness and oxygen transmittance were measured. The result is shown in a table 2. The thickness of a back thin film became thin, and this gas barrier film became that in which oxygen barrier property is inferior so that it may understand from now on.
[0032]
[A table 2]

比較例１

フィルム位置 (m)	膜　厚 (Å)	酸素透過度 (cc/m^2.24hr.atm)
２０００	５００	３．５
４０００	４２０	３．６
６０００	３２０	５．０
８０００	２２０	８．０
１００００	１２０	１６

[0033] The oxide thin film was formed with electron beam vacuum deposition on the PET film (the Toyobo Co., Ltd. make, E5100) of 12-micrometer thickness, using about 3-5mm particle-like the magnesium oxide (MgO, 99.5% of purity) and oxidation silicon (SiO2, 99.9% of purity) of magnitude as a source of example 2 vacuum evaporationo. MgO and SiO2 of a vacuum evaporationo material It put into the separate crucible. A thickness monitor irradiates the X-ray for excitation like an example 1, and can measure now the characteristic X ray of a thin film. The characteristic X ray of Mg (9.889A) and Si (7.129A) is measured, and it enabled it to apply feedback to the emission current of EB gun here. Film advance speed is about 100 m/min. It carries out, one set of EB gun is used as a source of heating, and it is MgO and SiO2. Each is heated by time sharing and it is MgO and SiO2. Bipolar membrane was

produced. The emission current of EB gun at that time is made into near 1.5A, and it is MgO and SiO2. The heating ratio was set to 1:1 and aim thickness was made into 500A. Thus, it sampled every 1000m from the vacuum evaporationo starting position of the produced gas barrier film, and a component analysis (ICP atomic absorption analysis) and thickness measurement were performed. This result is shown in a table 3. The long transparence gas barrier film with fixed presentation and thickness was obtained so that it may understand from now on.

[0034] Furthermore, to the compound thin film on this PET film, dry laminate of the non-extended polypropylene film (OPP film) with a thickness of 40 micrometers was carried out using 2 liquid hardening mold polyurethane adhesive (3 micrometers in thickness), and the gas barrier film for a package was obtained. Oxygen transmittance was measured after carrying out voile processing (80 degree-Cx 30 minutes) to this film for a package. This result is also shown in a table 3. The oxygen barrier property after voile processing was good, and the long transparence gas barrier film with a uniform oxygen barrier property was obtained in the length direction so that it may understand from now on.

[0035]

[A table 3]

実施例 2

フィルム位置 (m)	組成 (%)		膜 厚 (Å)	ボイル後の酸素透過度 (cc/m². 24hr. atm)
	MgO	SiO₂		
1000	15	85	500	2.0
2000	14.5	85.5	510	2.4
3000	15	85	500	2.1
4000	15	85	500	2.5
5000	14.5	85.5	510	2.2
6000	15	85	500	2.4
7000	15	85	495	2.7
8000	15	85	500	2.2

[0036] the example 2 of a comparison -- MgO and SiO2 using -- an example 2 -- the same -- carrying out -- MgO-SiO2 Although the thin film system gas barrier film was produced, aim thickness could be 500A, using a visible-ray permeability optical monitor as a thickness monitor. It sampled like the example 2, a component analysis and thickness measurement were performed, and the oxygen transmittance after voile processing was measured further. The result is shown in a table 4. The gap of a back presentation became large and, as for this gas barrier film, became what has the inadequate oxygen barrier property after voile so that it may understand from now on.

[0037]

[A table 4]

比較例２

フィルム位置 (m)	組成 (%)		膜 厚 (Å)	ボイル後の酸素透過度 (cc/m². 24hr. atm)
	ＭｇＯ	ＳｉＯ₂		
１０００	１５	８５	５００	１．０
２０００	１３	８７	４７０	１．２
３０００	１０	９０	４００	２
４０００	８	９２	３５０	６
５０００	５	９５	２８０	８
６０００	４	９６	２００	１０
７０００	４	９６	１８５	１０
８０００	３	９７	１５０	１５

[0038]
[Effect of the Invention] According to the manufacture method of the gas barrier film of this invention, or the manufacturing installation, the gas barrier film which the monitor of the thickness can be carried out also to the gas barrier film using a transparent and colorless thin film, a multiple oxide thin film, etc., therefore has a uniform property in the length direction is producible.

[Translation done.]

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CLAIMS

[Claim(s)]
[Claim 1] A manufacture method of a gas barrier film characterized by preparing an inorganic thin film on a plastics base material it runs to continuation, acting as the monitor of the thickness of the thin film concerned by measuring characteristic-X-ray reinforcement of at least one element among characteristic X ray of an element of the thin film presentation concerned released after making into an excitation state an atom which forms an inorganic thin film.
[Claim 2] A manufacturing installation of a gas barrier film which comes to have equipment which can act as the monitor of the thickness of the thin film concerned by measuring characteristic-X-ray reinforcement of at least one element among characteristic X ray of an element of a thin film presentation released after making into an excitation state an atom which forms the inorganic thin film concerned in production of a gas barrier film which prepares an inorganic thin film on a plastics base material it runs to continuation.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the schematic diagram of one example of the gas barrier film manufacturing installation of this invention.
[Drawing 2] It is the enlarged view of the thin film thickness monitor portion of this invention.
[Description of Notations]
1 It Begins to Wind and is Roll.
2 Rolling-Up Roll
3 Chilled Roll
4 Plastics Base Material
5 Electron Gun (EB Gun)
6 Crucible
7 Secondary Electron Trap
8 Exhaust Air System
9 Adhesion-proof Board
10 Source Material of Vacuum Evaporationo
11 X Line Source for Excitation
12 Characteristic-X-Ray Detector
13 Shutter
14 Collimator
15 Gas Barrier Film
16 Inorganic Thin Film
17 X-ray for Excitation
18 Characteristic X Ray

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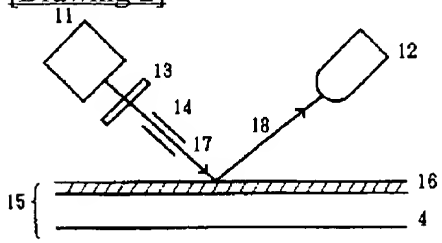
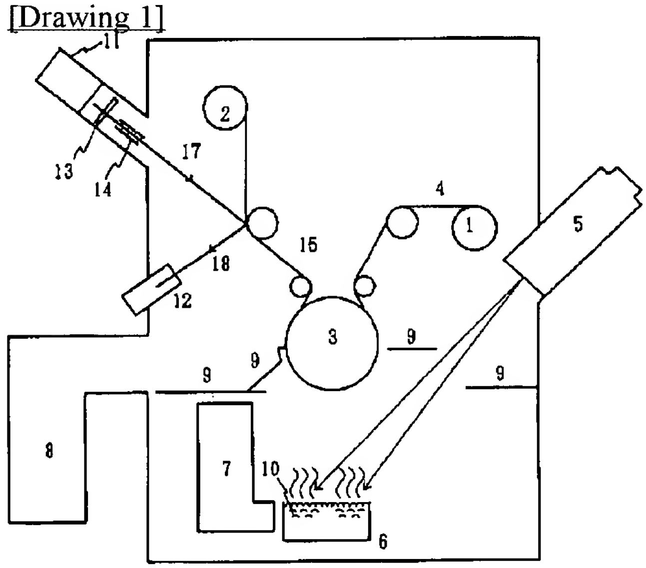
DRAWINGS

[Drawing 2]



[Drawing 1]



1	巻き出しロール	1 0	蒸着源材料
2	巻き取りロール	1 1	励起用Ｘ線源
3	チルロール	1 2	特性Ｘ線検出器
4	プラスチック基材	1 3	シャッター
5	電子銃（ＥＢ銃）	1 4	コリメーター
6	るつぼ	1 5	ガスバリアフィルム
7	二次電子トラップ	1 7	励起用Ｘ線
8	排気系	1 8	特性Ｘ線
9	防着板		

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